

# Overview of Advanced Characterization within the Powertrain Materials Core Program\*

\*Thrust 4A under the Powertrain Materials Core Program (PMCP)

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**Arun Devaraj**, Bharat Gwalani, Libor Kovarik, Mathew Olszta, Dalong Zhang, PNNL

2020 DOE Vehicle Technologies Office  
Annual Merit Review

June 4, 2020

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# Program Overview: VTO Powertrain Materials Core Program

## Timeline/Budget

- Lab Call Award: July 2018
- Budget: \$30M/5 years
- Program Start: Oct 2018
- Program End: Sept 2023
- 30% Complete

## Barriers

- Increasing engine power densities & higher efficiency & cleaner engines; resulting in increasingly extreme materials demands (increased pressure and/or temperature)
- Affordability of advanced engine materials & components
- Accelerating development time of advanced materials
- Scaling new materials technologies to commercialization

## FY20 Program Research Thrusts

### FY20 Budget

### Participating Labs

#### 1. Cost Effective LW High Temp Engine Alloys

\$1.05M

ORNL

#### 2. Cost Effective Higher Temp Engine Alloys

\$1.525M

ORNL, PNNL

#### 3. Additive Manufacturing of Powertrain Alloys

\$1.075M

ORNL

#### 4A. Advanced Characterization

\$1.025M

ORNL, PNNL, ANL

#### 4B. Advanced Computation

\$0.60M

ORNL

#### 5. Exploratory Research: Emerging Technologies

\$0.75M

ORNL, PNNL, ANL

## Partners

- Program Lead Lab
  - Oak Ridge National Lab (ORNL)
- Program Partner Labs
  - Pacific Northwest National Lab (PNNL)
  - Argonne National Lab (ANL)

# Overview of Advanced Characterization within the Powertrain Materials Core Program




## Timeline

- Project start: Oct 2018
- Project end: Sep 2023
- Percent complete: 30%

## Barriers

- Development time.
- Numerous variables to test

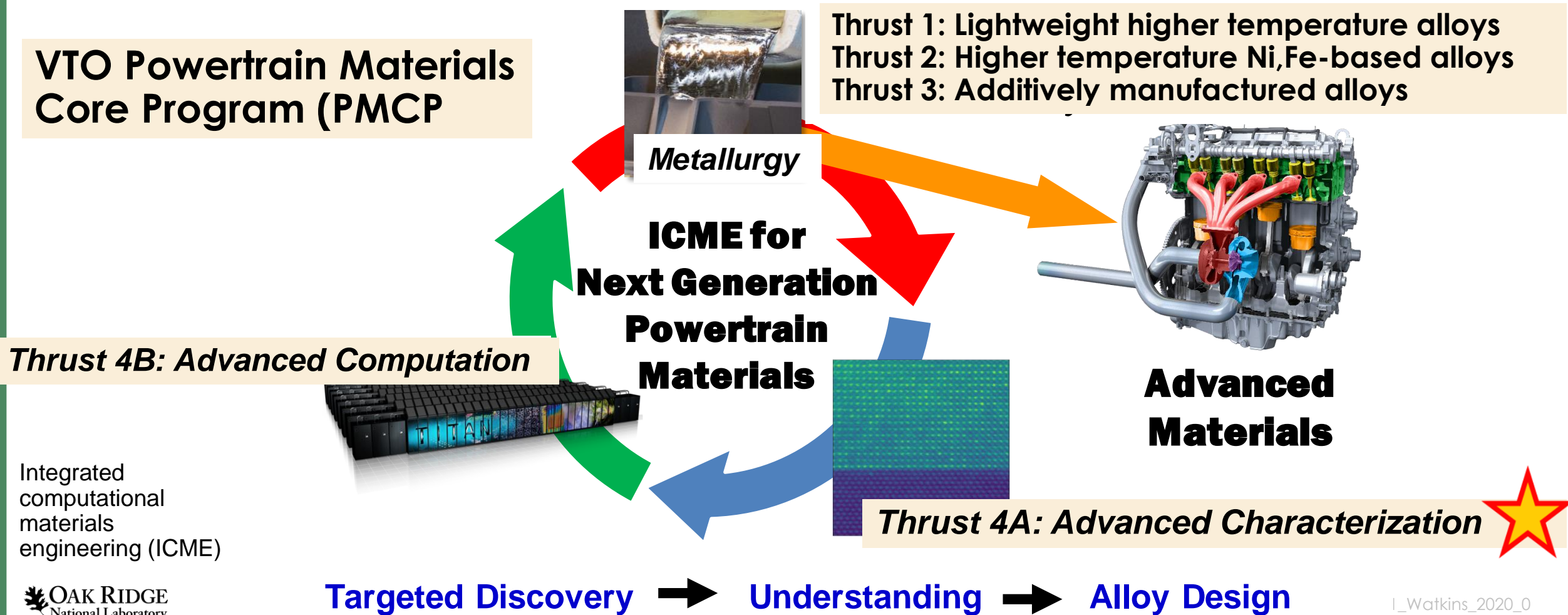
## Budget & Partners

 Lead			Total
\$425k	\$300k	\$300k	FY20: \$1.025M
\$450k	\$300k	\$300k	FY19: \$1.05M







# Relevance

- All advanced and fuel-efficient powertrain designs – all share a common barrier:
  - Economical material performance at high temperature and pressures/loads
- Accelerate alloy development:

## VTO Powertrain Materials Core Program (PMCP)




# Milestones

Thrust	Task 4A: Advanced Characterization	National Lab Ownership
1-3	Q1. Demonstrate and evaluate the effectiveness and sensitivity of collecting quantitative elemental maps with electron probe microanalysis using the new PROBE and Pathfinder collection software for quantitative understanding (w/Thrusts 1-3). <b>Complete.</b>	
1	Q2. Submit a manuscript describing in-situ heating studies with Xe plasma FIB sample preparation of an AlCu alloy and precipitate processes (w/Thrust 1). <b>Complete.</b>	
2	Q3. Complete scanning transmission electron microscopy (STEM) analysis of selected prototype ferrous and nickel- based alloys from Thrust 2 to determine precipitate distribution and structures (w/Thrust 2). <b>On-track.</b>	
1	Q3. Characterize at least 2 light weight alloys for engine applications. <b>On-track.</b>  (NOTE: Milestone inserted by VTO into EERE site)	
1	Q4a. Submit a manuscript on the synchrotron analysis of the theta-theta prime phase transformation in cast AlCuMnZr alloys (with Argonne & Thrust 1). <b>On-track.</b>	
1	Q4b. Submit a manuscript describing in-situ annealing with atom probe tomography of an Aluminum alloy and the related precipitate processes (with PNNL & Thrust 1). <b>On-track.</b>	

# Strategy for Thrust4A

- Conceptually innovative, advanced characterization (and advanced computation) is elevated & protected by separate funding to support the **three** development thrusts:

-  – **Thrust 1: Cost Effective Lightweight High Temp Engine Alloys**
-  – **Thrust 2: Cost Effective Higher Temp Engine Alloys**
-  – **Thrust 3: Additive Manufacturing of Powertrain Alloys**

to take full advantage of the unique advanced characterization tools at **three** national laboratories



- Funds allocated via one-page proposals:
  - Goal & strategic importance
  - Research plan & team
  - Review committee approval

# Thrust 4A Approach: Matrix of experts with unique tools



Matrix



## Synchrotron X-Rays



Diffraction  
SAXS  
Tomography



## Electron Microscopy



## Electron Microscopy



## Atom Probe



## Atom Probe



## In-situ stages, environments



## Neutrons



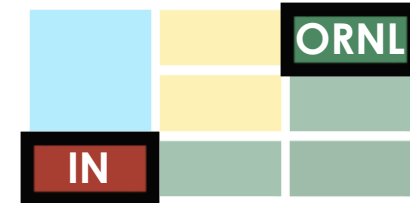
Diffraction  
SANS  
Tomography



## Electron MicroProbe

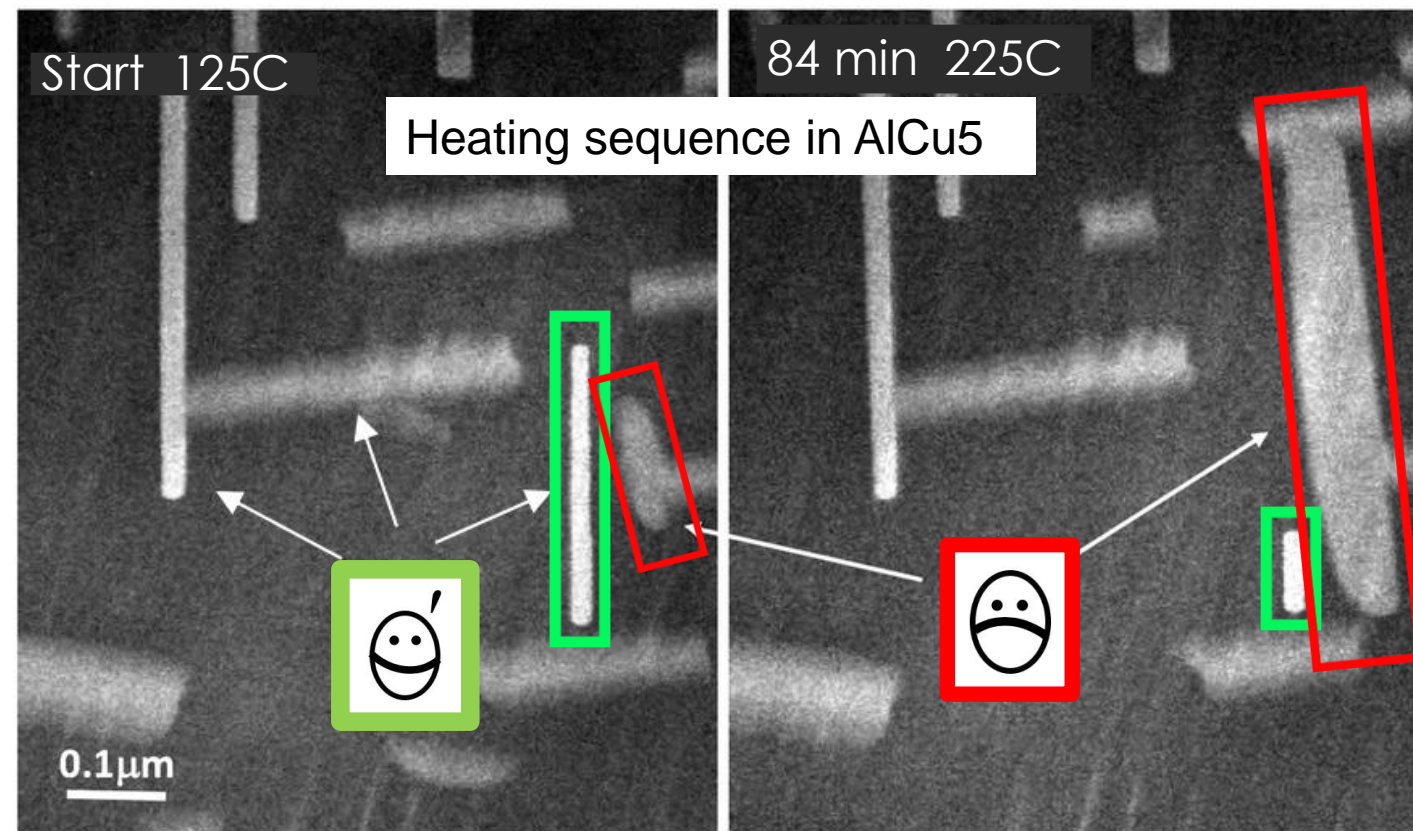


# ORNL scanning transmission electron microscopy (STEM) studies precipitate (ppt) growth & dissolution **in-situ, at temp, in real time** to understand strength loss of ORNL's aluminum alloys



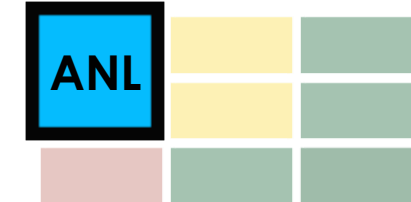
**Matrix**  
Larry Allard, ORNL  
Ryan Dehoff, ORNL  
Amit Shyam, ORNL  
Subtask 1A

- Accelerates alloy development
- Discovering new phenomena we had not anticipated
- Cross-cutting technique, many applications
- Here understanding precipitate (ppt) "life cycle"



$\theta'$  ppts provide high temp (HT) strength, yet are consumed in a transition to  $\theta$  ppt with time at temp. Understanding and controlling this transition is key to commercial applications

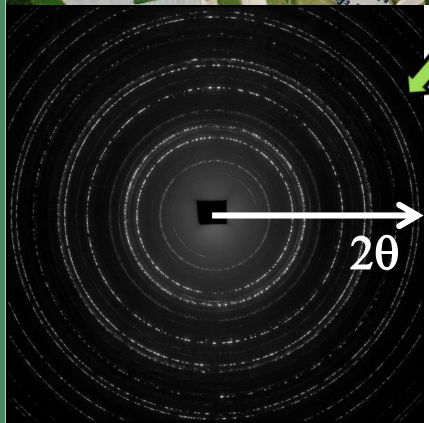
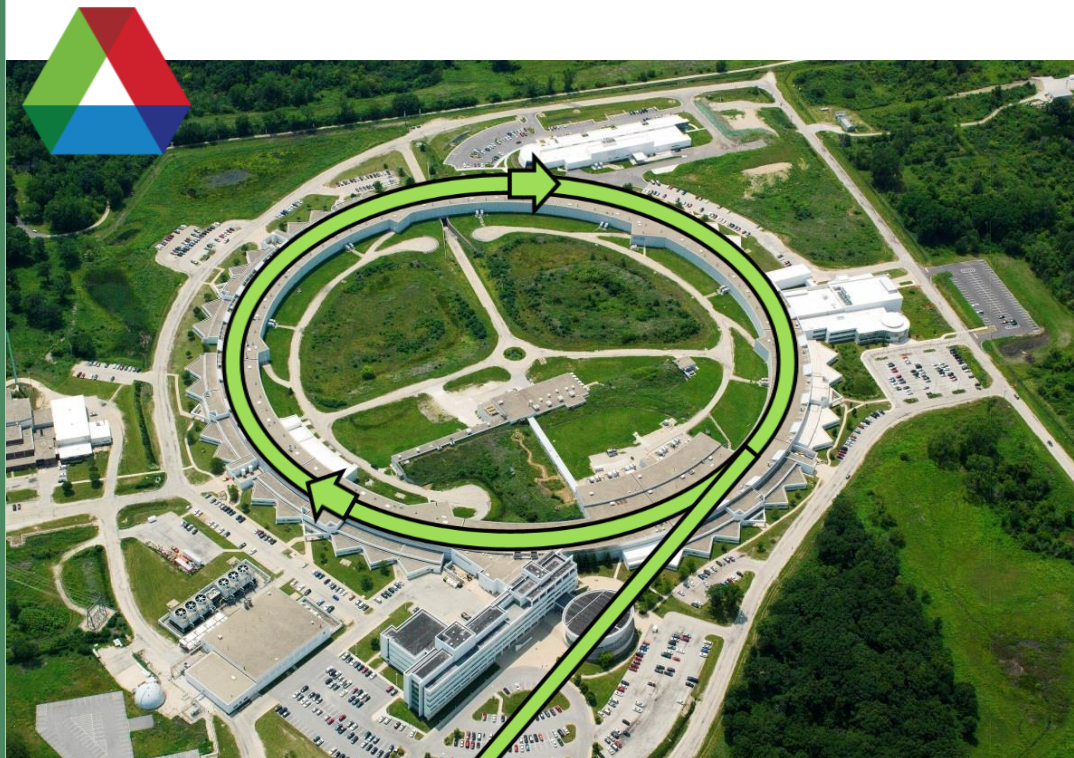
# “Bulk” quantification of trace precipitate’s fraction & critical phase transition in an ORNL cast Al alloy required the Advanced Photon Source at ANL



Matrix



Dileep Singh, ANL  
Andrew Chang, ANL  
Lianghua Xiong, ANL  
Amit Shyam, ORNL  
Thomas Watkins, ORNL  
Subtask 1A

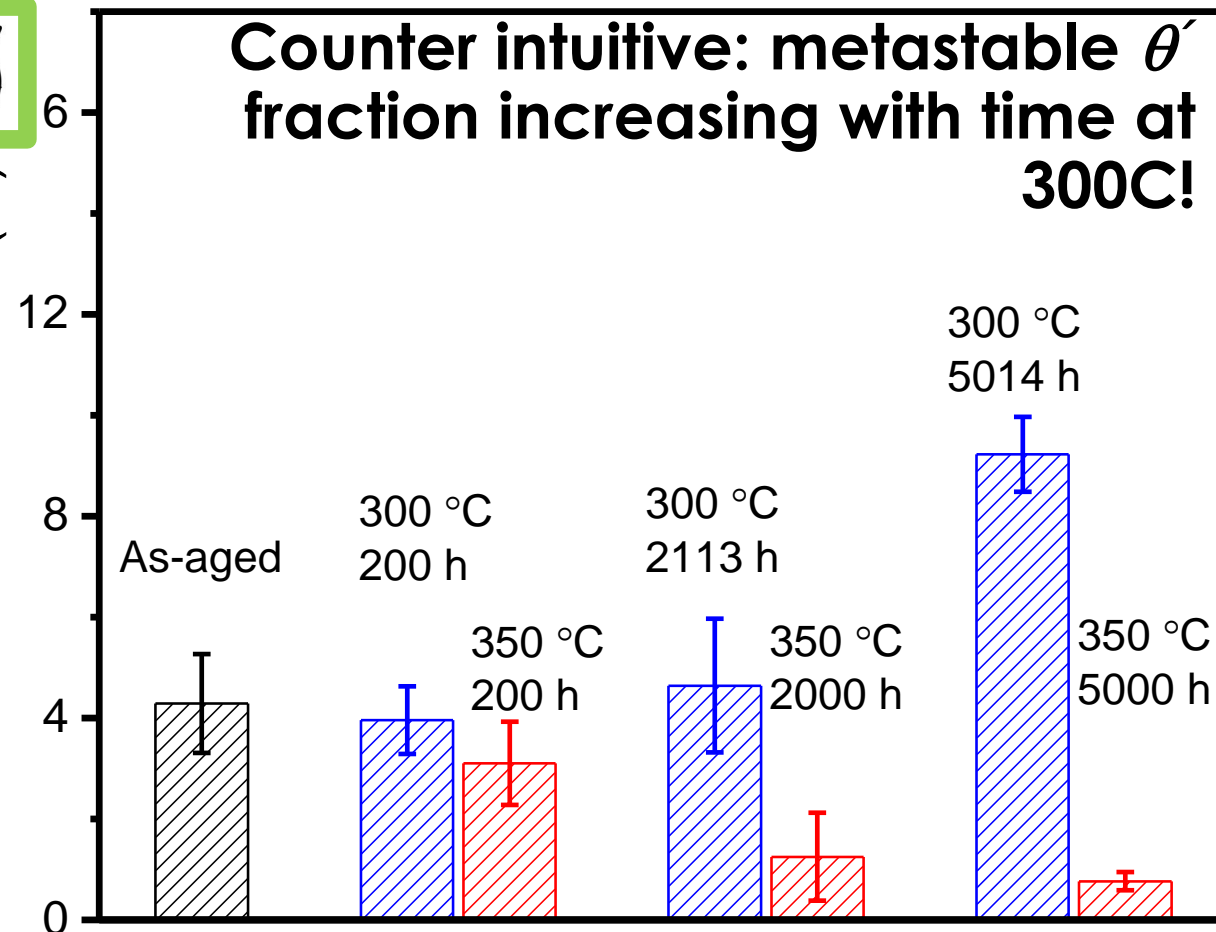


To preserve HT strength means stopping  $\theta'$  transforming to  $\theta$ , fraction trends linked to microstructure



Theta Prime fraction (%)

Counter intuitive: metastable  $\theta'$  fraction increasing with time at 300C!



# Milestone 2: Manuscript submitted for Xe Plasma Focused Ion Beam study

Jon Poplawsky, ORNL  
Larry Allard, ORNL  
Amit Shyam, ORNL  
Subtask 1A

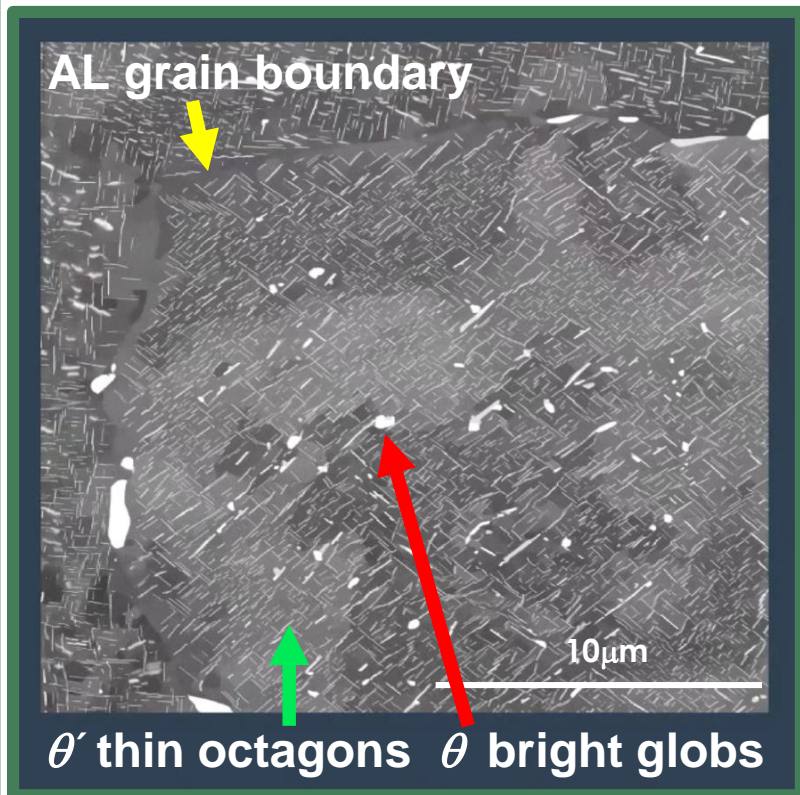


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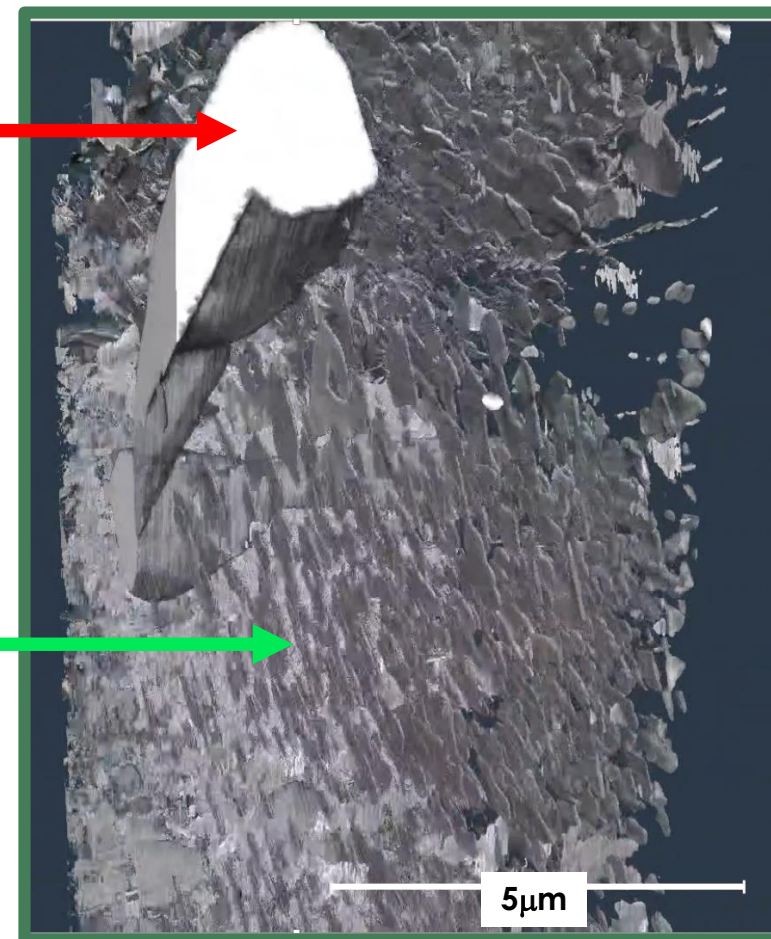
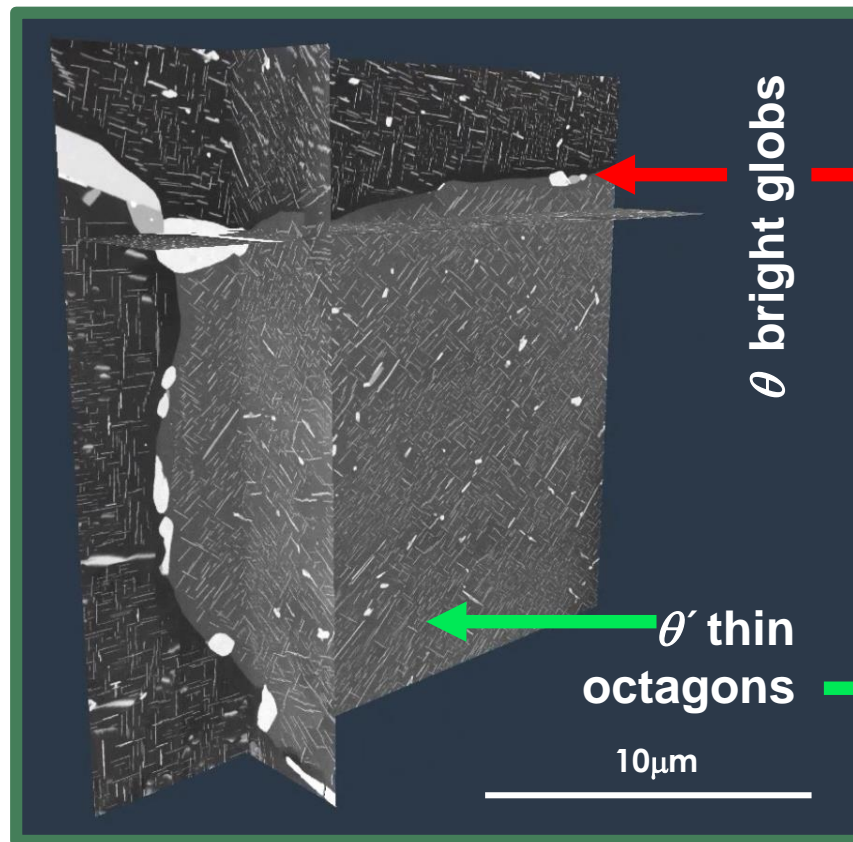
Matrix

Tomographic sections show Al7Cu alloy exposed at 300°C for 200 hours,  $\theta'$ -Al2Cu still stable (thin octagons)

- Quantify precipitate sizes, shapes, spacing & distributions
- Observe evolution of ppts

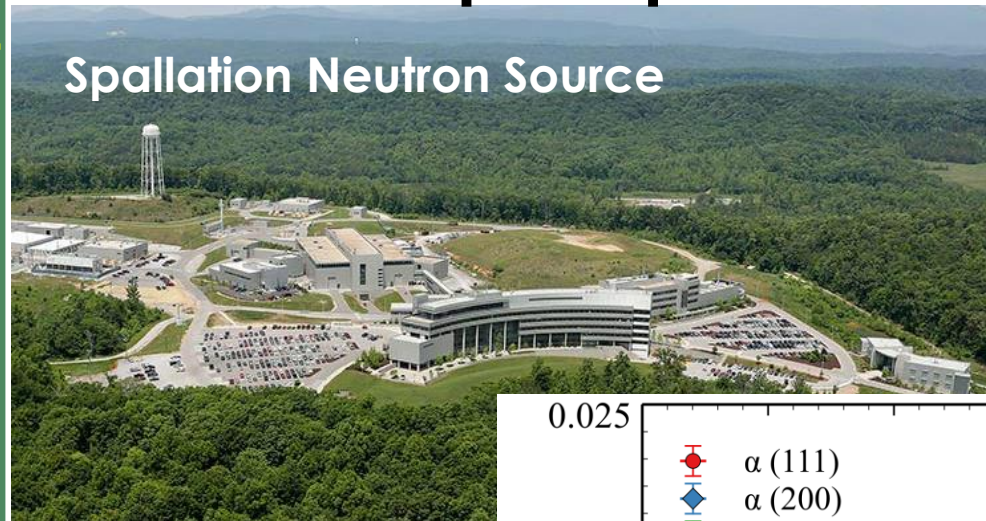
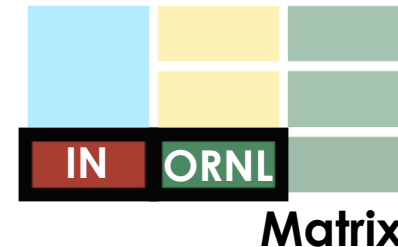


- ~6X faster FIB rate than Ga
- No Ga "contamination"
- Greatly reduced sample damage

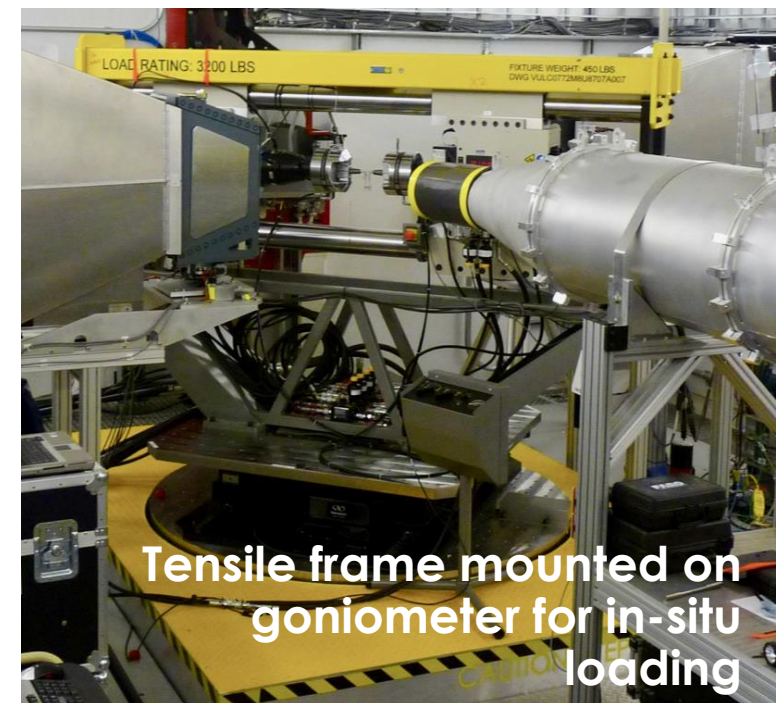
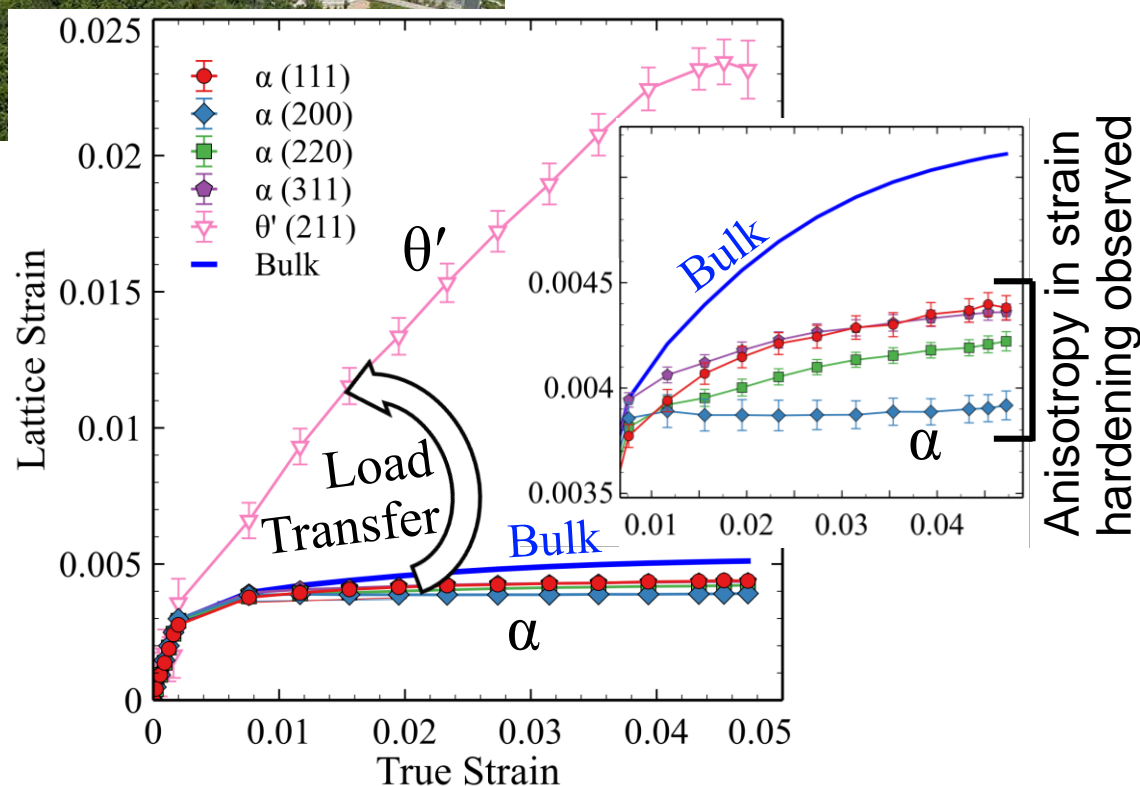


# ORNL SNS: Neutron diffraction with in-situ loading shows load transfer from aluminum matrix to $\theta'$ precipitates

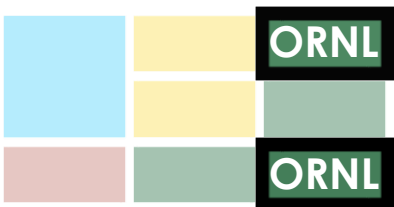
Brian Milligan, ORNL  
Amit Shyam, ORNL  
Dong Ma, ORNL  
Subtask 1B



- Matrix starts deforming plastically but the precipitates are still deforming elastically; model agrees
- Load transfer efficient in 200 oriented grains, least in 111 oriented; All others in between.

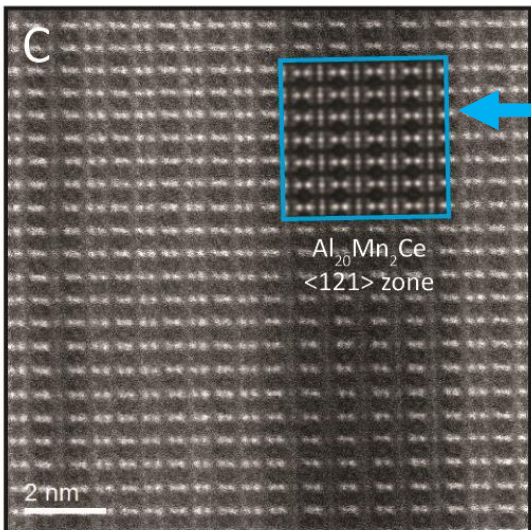
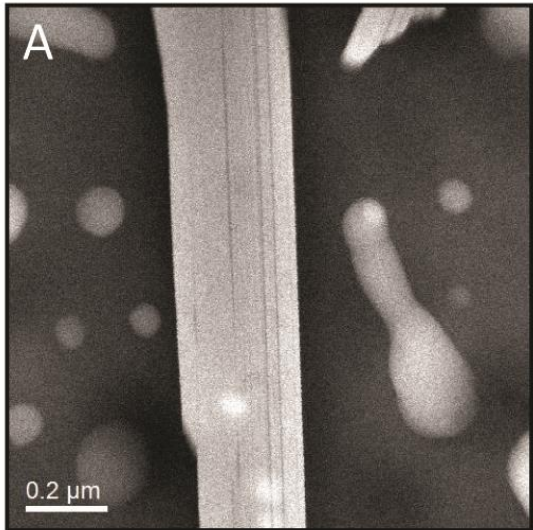


# ORNL STEM validates phase diagrams predicted by Integrated computational materials engineering (ICME).

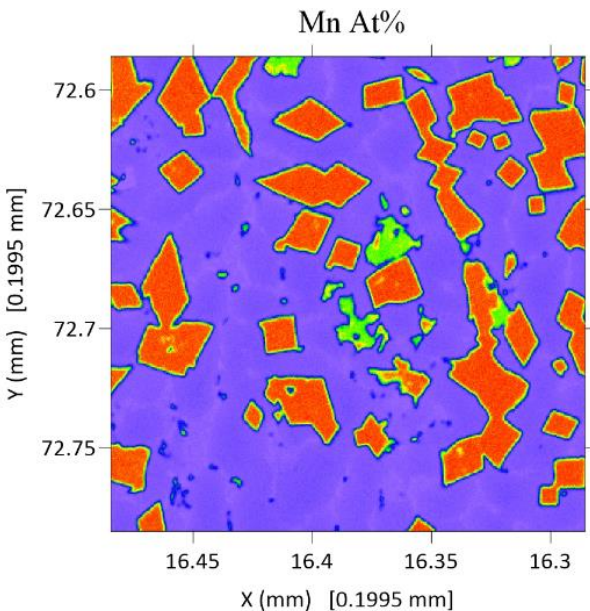


Matrix

Michael Lance, ORNL  
 Amit Shyam, ORNL  
 Alex Plotkowsky, ORNL  
 Ryan Dehoff, ORNL  
 Ying Yang, ORNL  
 Larry Allard, ORNL  
 Sumit Bahl, ORNL  
 Kevin Sisco, UTK  
 Subtask 3A



- STEM images of new phase  $\text{Al}_{20}\text{Mn}_2\text{Ce}$
- Milestone 1: Electron probe microanalysis (EPMA) map of phases & quantifies elemental compositions of alloys for additive manufacturing

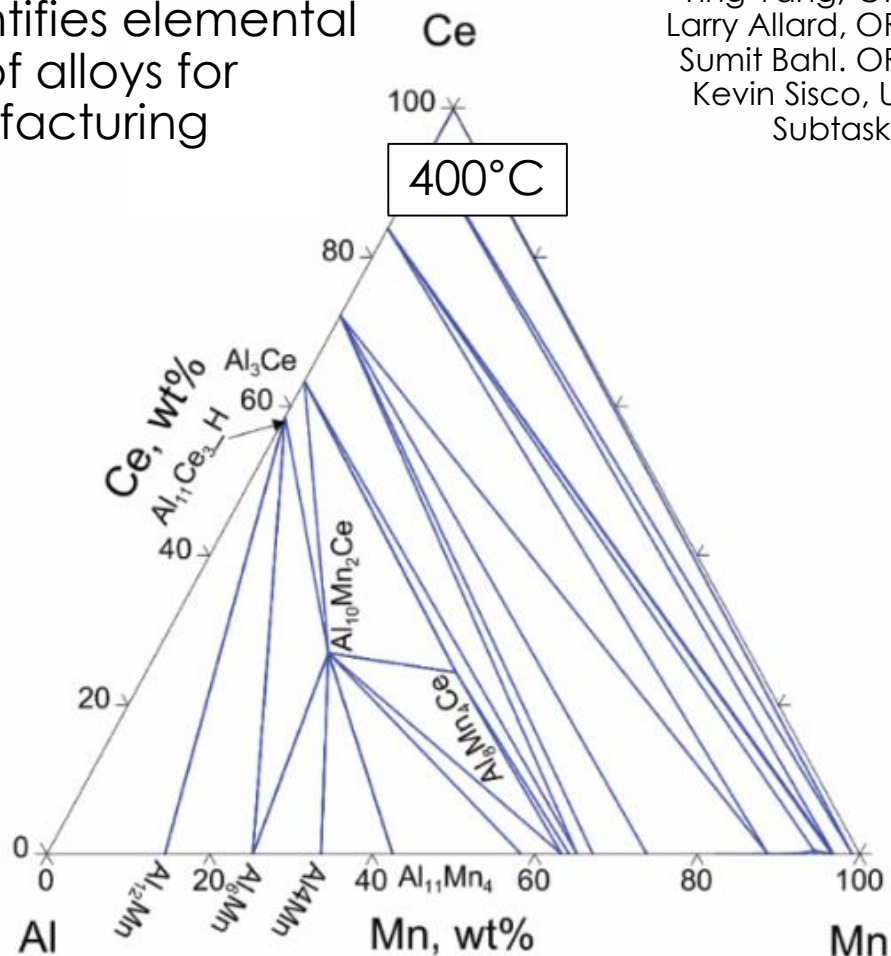


**RED**  $\text{Al}_{10}\text{Mn}_2\text{Ce}$ ,  
 strengthening phase,  
 high Mn

**GREEN**  $\text{Al}_{20}\text{Mn}_2\text{Ce}$ ,  
 "medium" Mn

**PURPLE** AL matrix,  
 No Mn

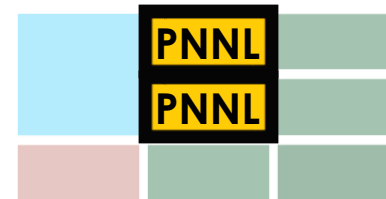
\*Relative ~5 at%;  
 detection limit 0.05 at%



# PNNL STEM & APT revealed structure & composition of primary precipitates within ORNL's heat treated Ni based valve alloy

T2

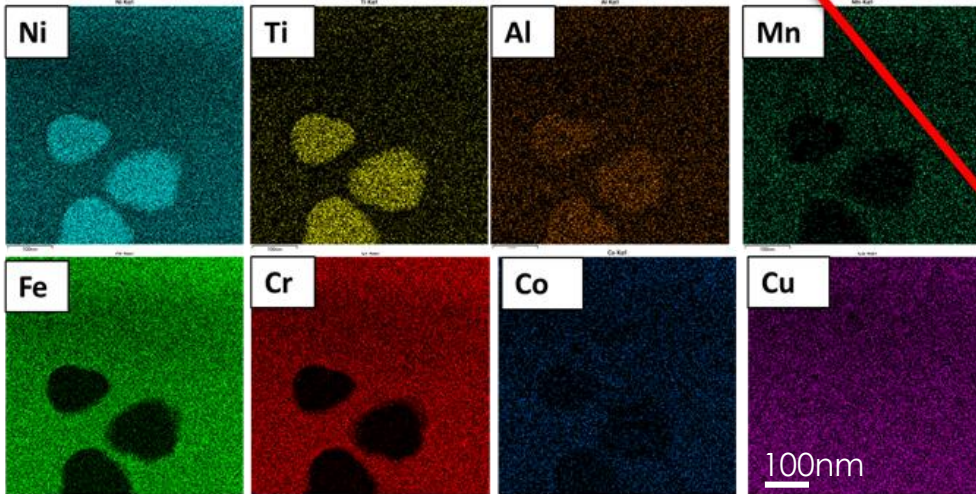
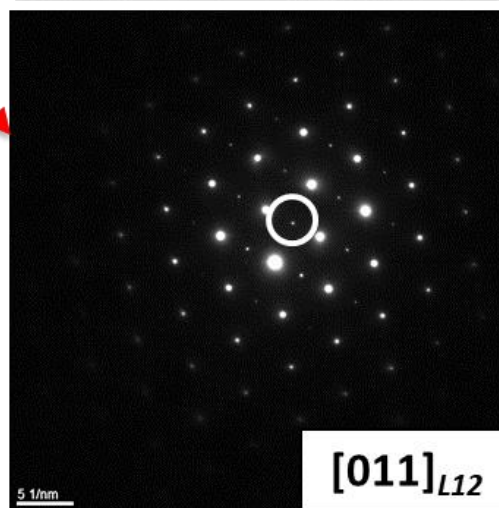
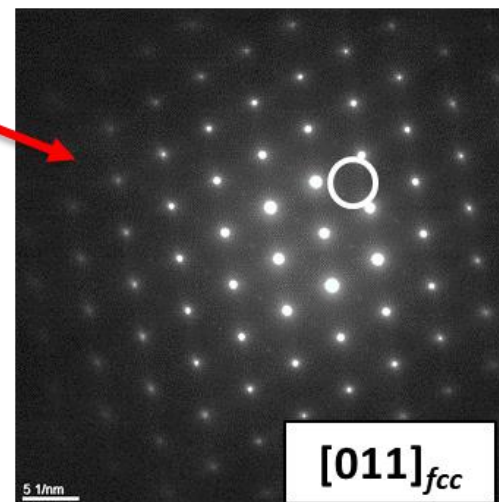
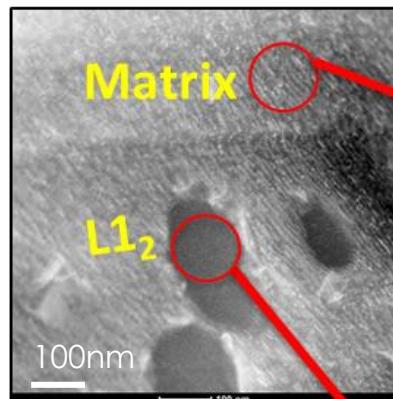
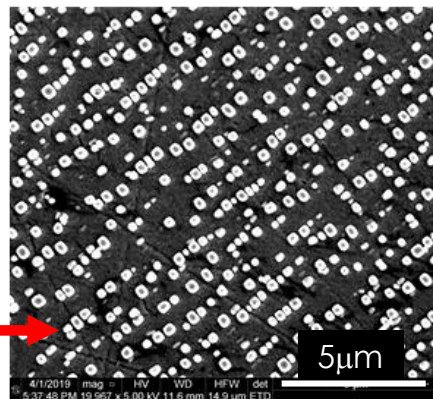
Arun Devaraj, PNNL  
Bharat Gwalani, PNNL  
Libor Kovarik, PNNL  
G. Muralidharan, ORNL  
Subtask 2A1



Pacific Northwest  
NATIONAL LABORATORY

## STEM provide structure and chemistry

• Squares are  $\gamma'$  ppts.

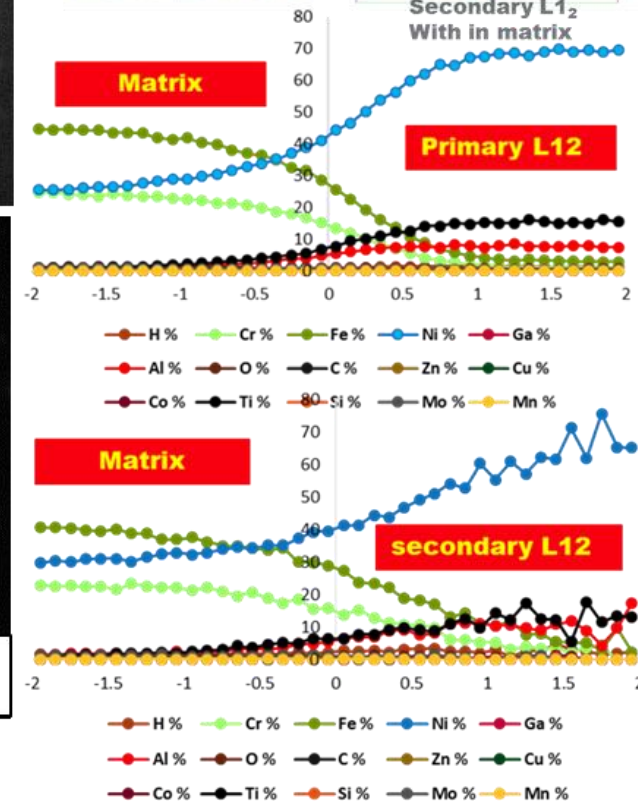
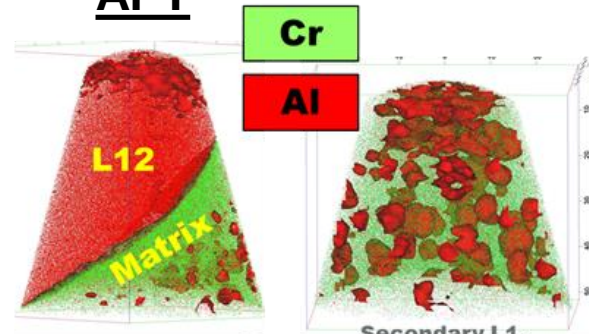


• Atom probe tomography (APT, far right) provides composition across interfaces  $\gamma'$  ppt. &  $\gamma$  matrix

Aged+ 900°C/250h  
Faint L1<sub>2</sub> super-lattice spots, Ni<sub>3</sub>(Al,Ti), seen in matrix as well.

Matrix

APT



# ANL USAXS Beamline, APS 9-ID-C, utilized in-situ heating to observed particles growing within ORNL's Ni based valve alloy

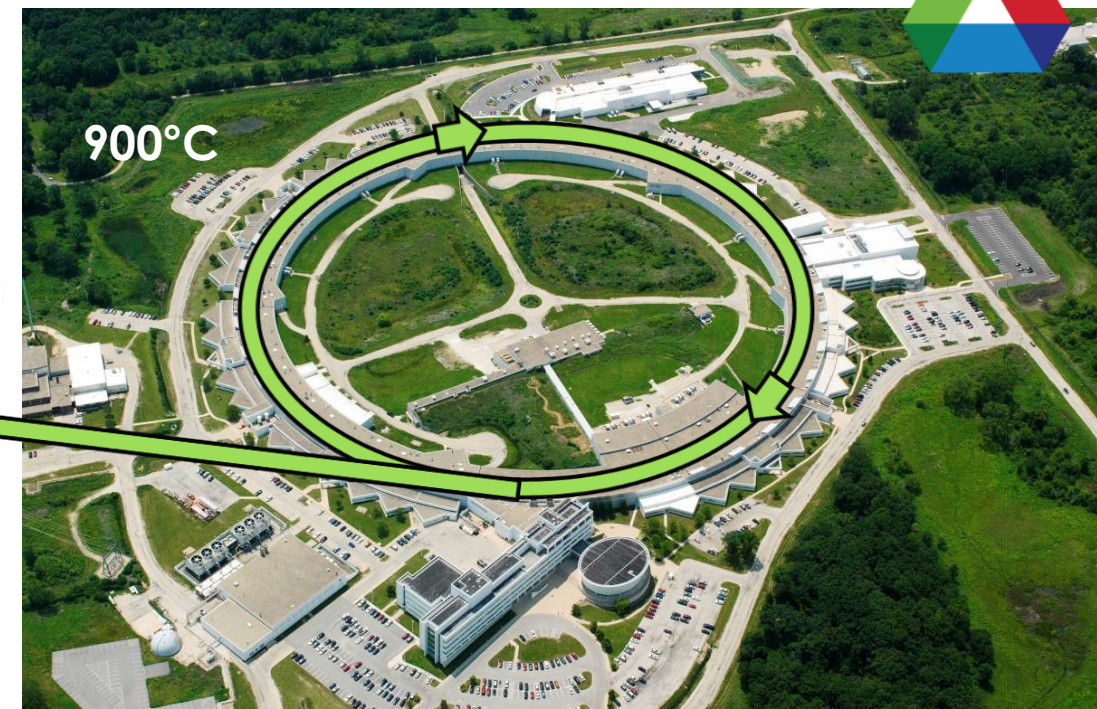
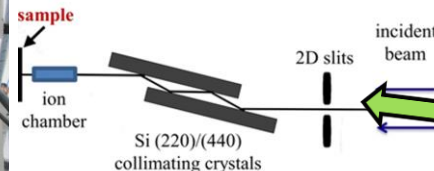
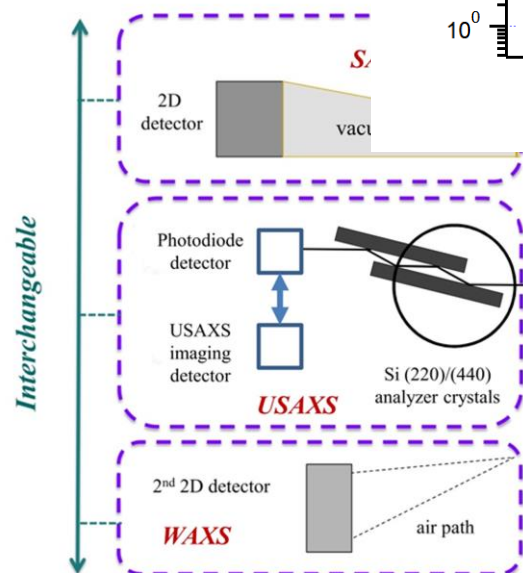
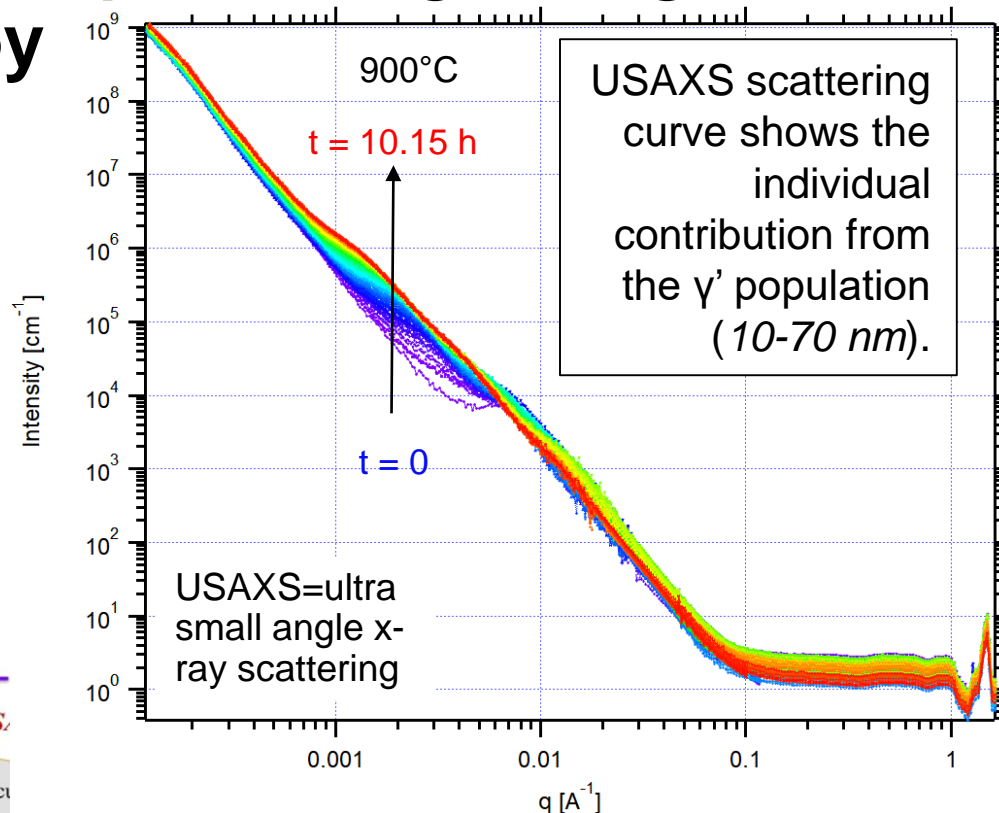


**Matrix**

Jan Ilavsky, ANL  
Matthew Firth, ANL  
G. Muralidharan, ORNL  
Subtask 2A1



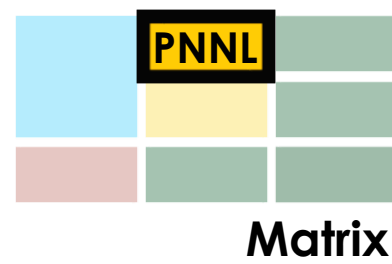
**Understanding sizes of  $\gamma'$  ppts is critical for understanding & controlling alloy strength**



# PNNL Microscopy: Multi-Phase Identification within ORNL's Creep-Ruptured Cast AFA Alloy Supported Verification of Alloy Design Study

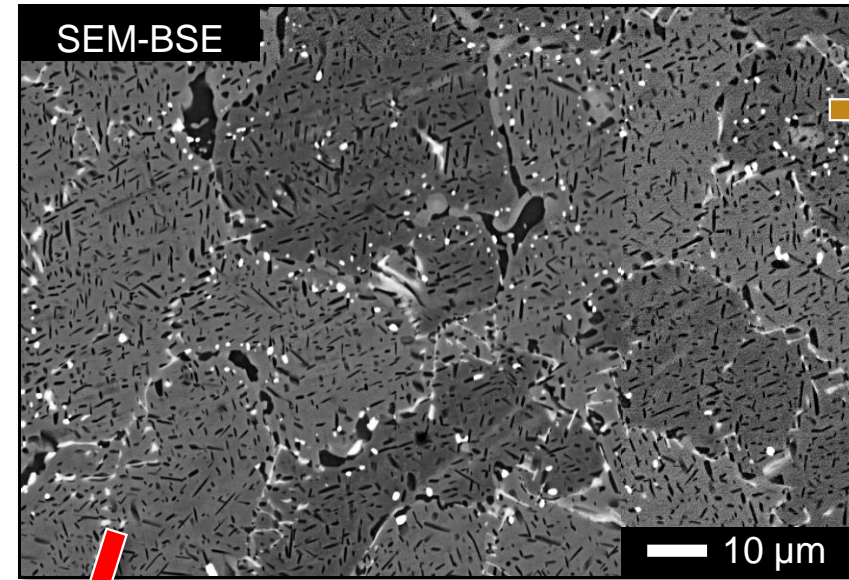


Arun Devaraj, PNNL  
Bharat Gwalani, PNNL  
Libor Kovarik, PNNL  
M. Brady, ORNL  
Y. Yamamoto, ORNL  
G. Muralidharan, ORNL  
(Subtask 2B1, PMCP)



- Cast Alumina Forming Austenitic (AFA) alloy development
  - Target high-temperature components above 900-950°C (e.g. exhaust manifold)
  - Multi second-phase precipitation strengthening designed through ICME
  - Feed back detailed parameters (type, size, volume fractions, etc.) to reveal property-microstructure relationship

Cast AFA (AFA2\*), 900°C/50MPa/421h



EDS elemental maps

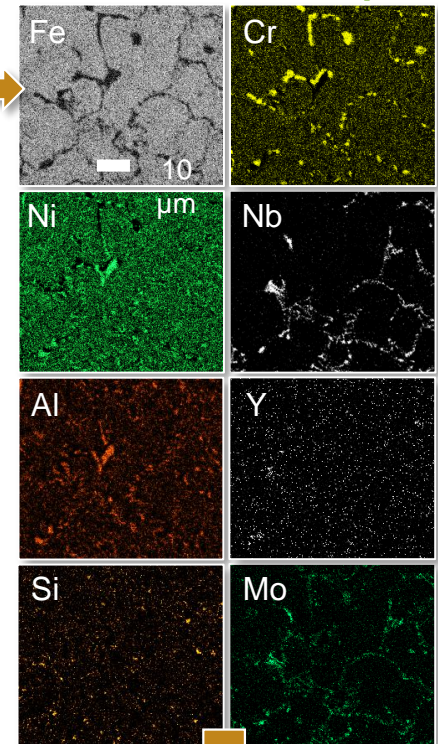
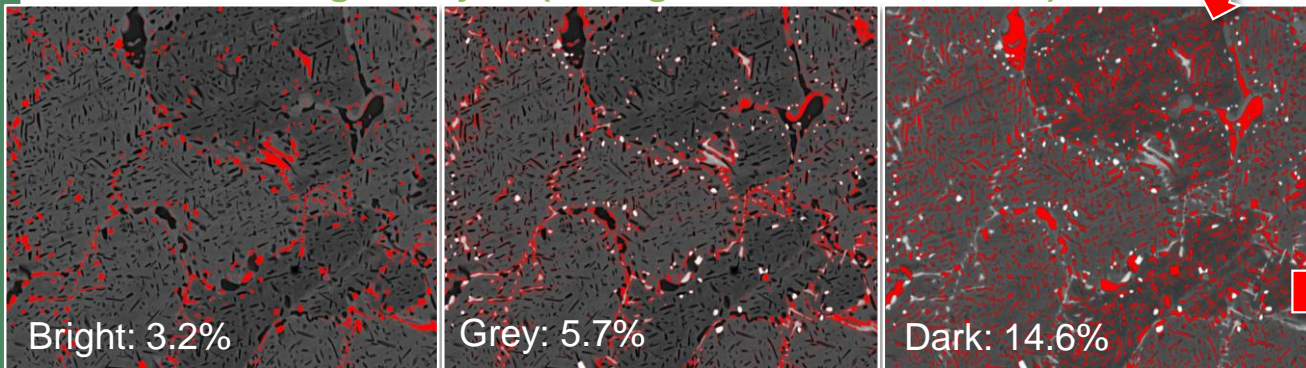


Image analysis (through contrast distinction)



\* AFA2: cast alumina-forming austenitic stainless steel, Fe-25Ni-15Cr-4Al-Nb-C base

Identified phase fraction:

- Laves-Fe<sub>2</sub>(Nb,Mo) [Bright phase]: 3.2%
- M<sub>23</sub>C<sub>6</sub> [Grey phase]: 5.7%
- B2-NiAl [Dark rich phase]: 14.6%

→ Evaluate the agreement/gap from the prediction

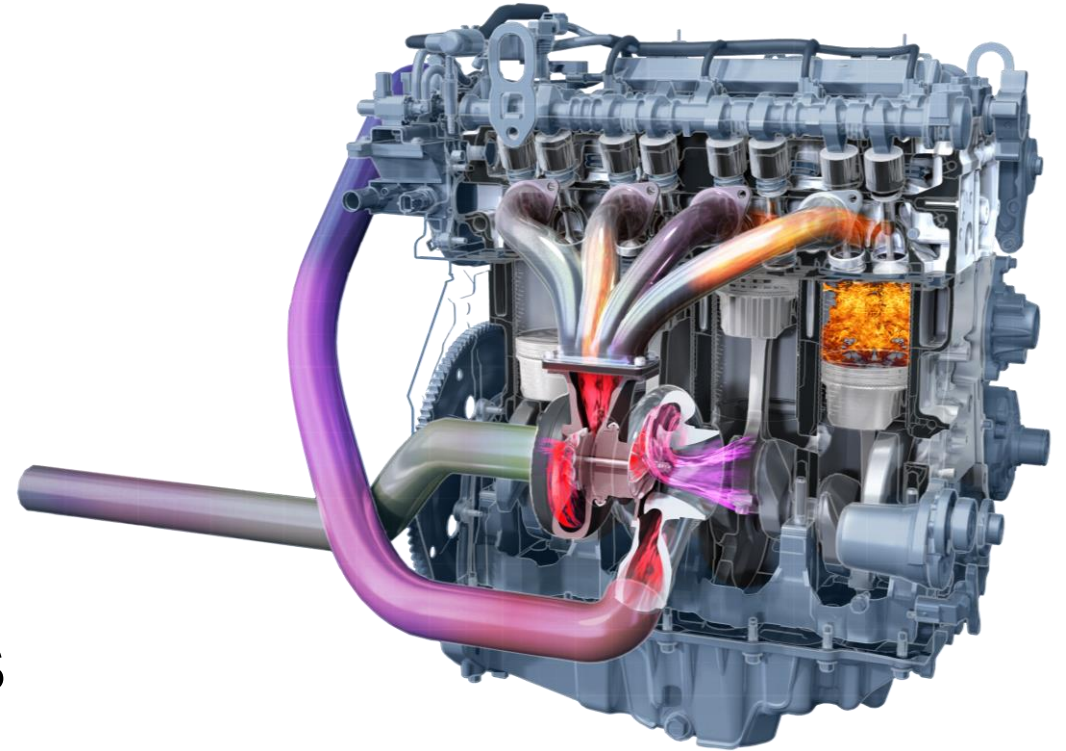
# Collaboration and Coordination with Other Institutions



- Argonne National Laboratory
  - Dileep Singh
  - Lianghua Xiong
  - Andrew Chuang
  - Jan Ilavsky
  - Matthew Frith
- Pacific Northwest National Laboratory
  - Arun Devaraj
  - Bharat Gwalani
  - Mathew Olszta
  - Libor Kovarik
  - Dalong Zhang
- Protochips Inc. (Raleigh, NC)
  - E-chip heaters for in situ experiments

# Responses to Previous Year Reviewer's comments

- Project was not reviewed last year



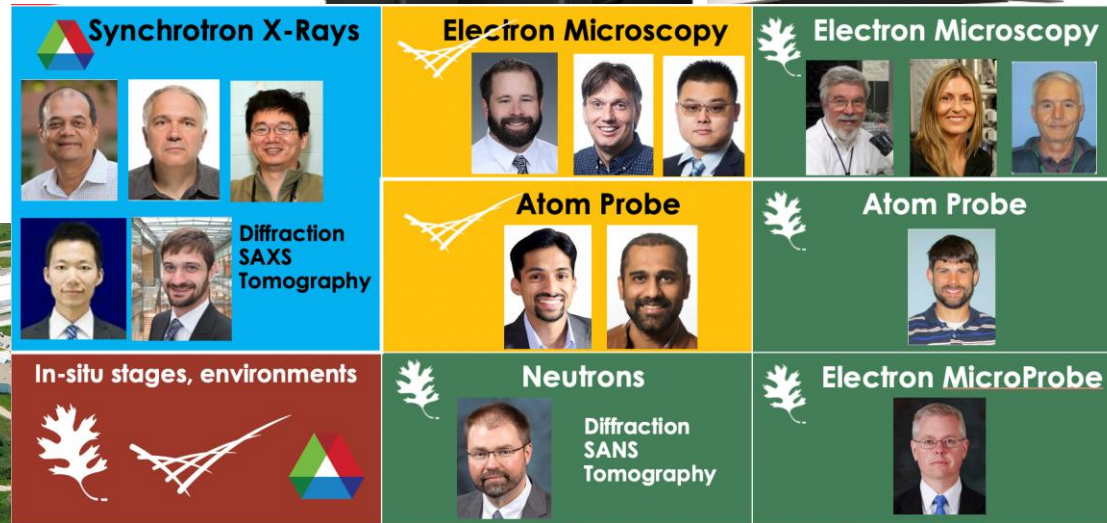
## Remaining Challenges and Barriers

- Prioritization of advance characterization requests
- Learning to integrate characterization data with ICME and advanced analytics within Thrust 4B

# Proposed Future Research

- ORNL: In-situ HT STEM studies, correlate thin-foil precipitate evolution to bulk material precipitate evolution, and thereby significantly accelerate alloy development and discovery
- ANL Synchrotron:
  - In-situ loading and tomography studies of valve alloys at temperature with new flexible in-situ heating & loading system being developed through Thrust 5.
  - Diffraction study of the thermal stability of new light weight alloy systems, e.g. Al-Ni, to help validate model
- PNNL: Characterize microstructure and fine precipitates in developmental piston alloys with advanced scanning transmission electron microscopy.

# Summary: *Three National Labs working together to address national applied materials needs with a suite of world-class materials characterization tools*

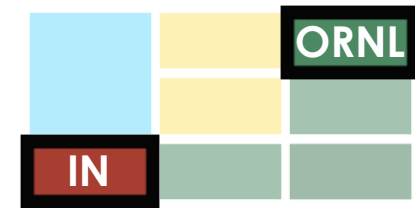


**Matrix of  
16+ experts w/  
Unique tools**



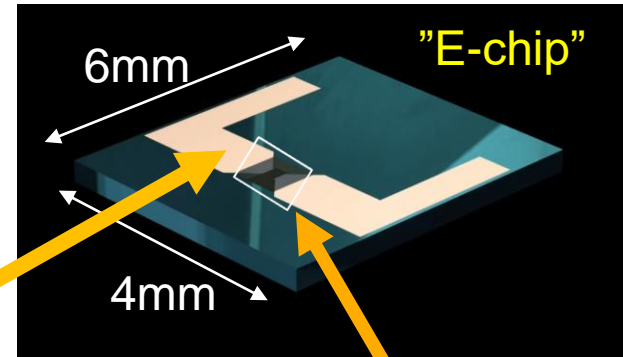
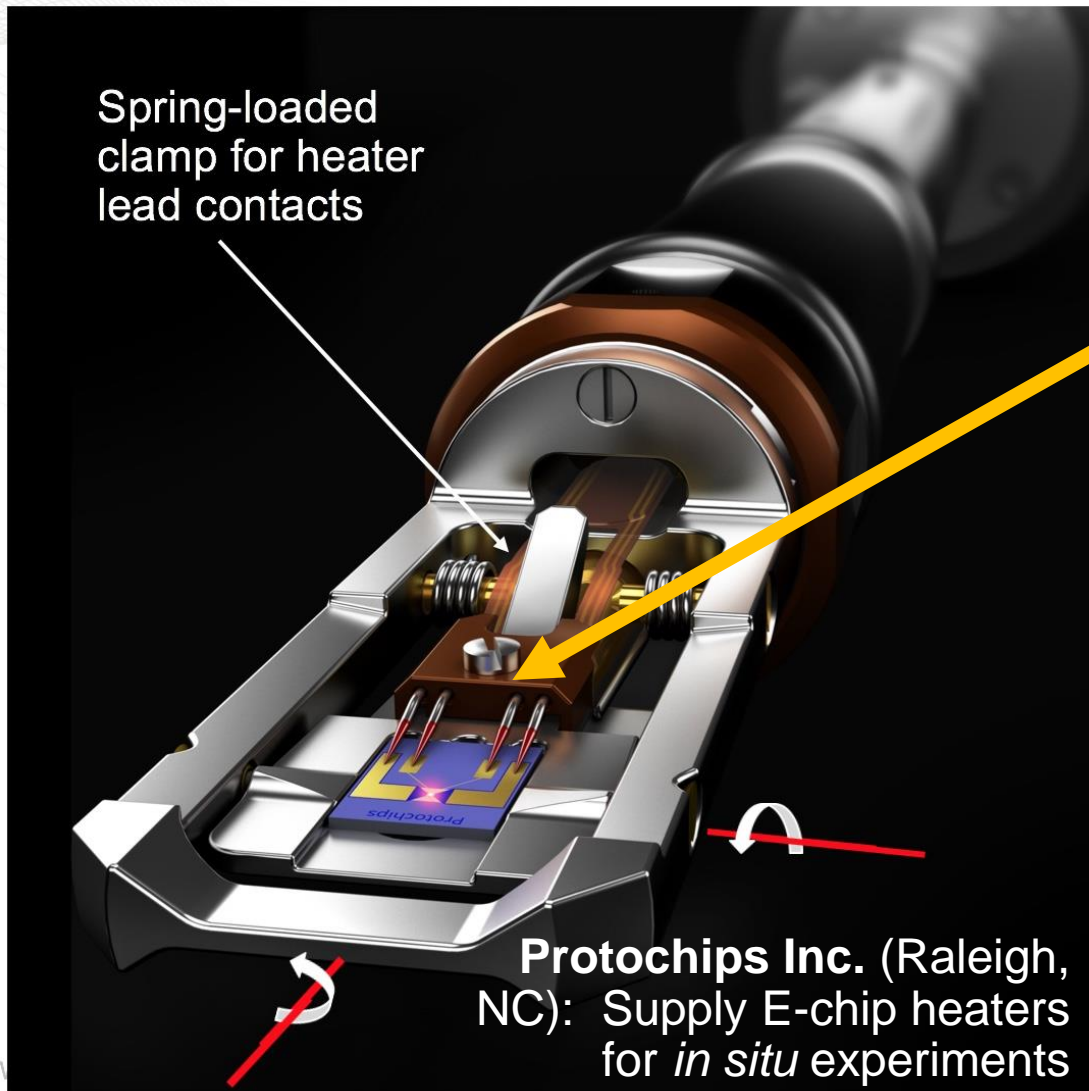
# Technical Back-Up Slides

# ORNL microscopy develops an in-situ heater & techniques for scanning transmission electron microscopy (STEM)

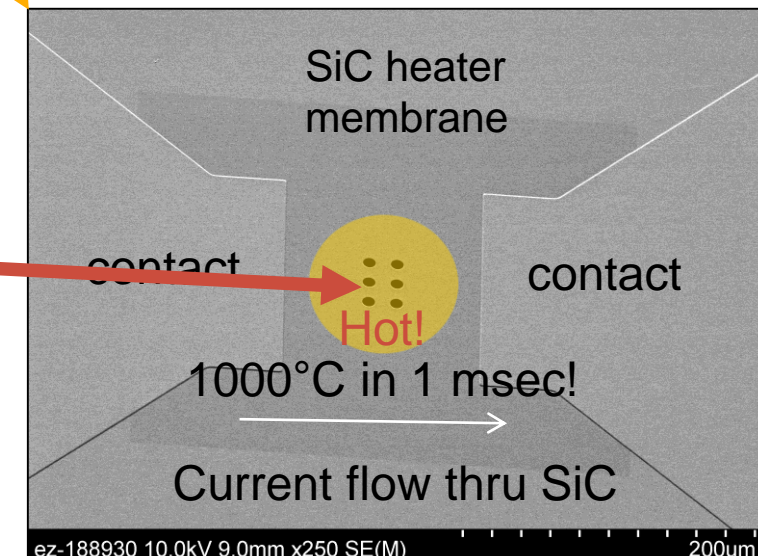
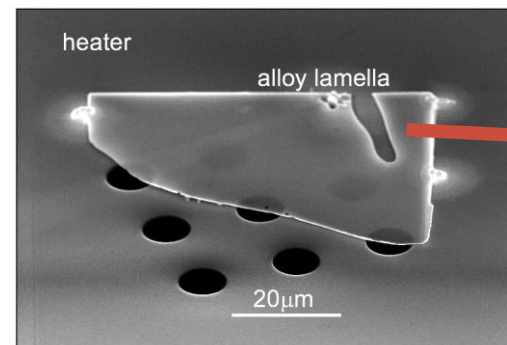


Matrix

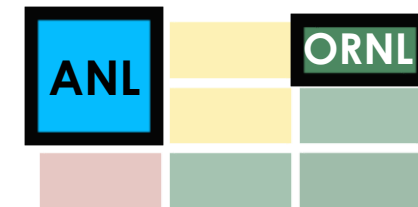
Larry Allard, ORNL  
Ryan Dehoff, ORNL  
Amit Shyam, ORNL  
Subtask 1A



Xe-PFIB sample section placed on hot stage

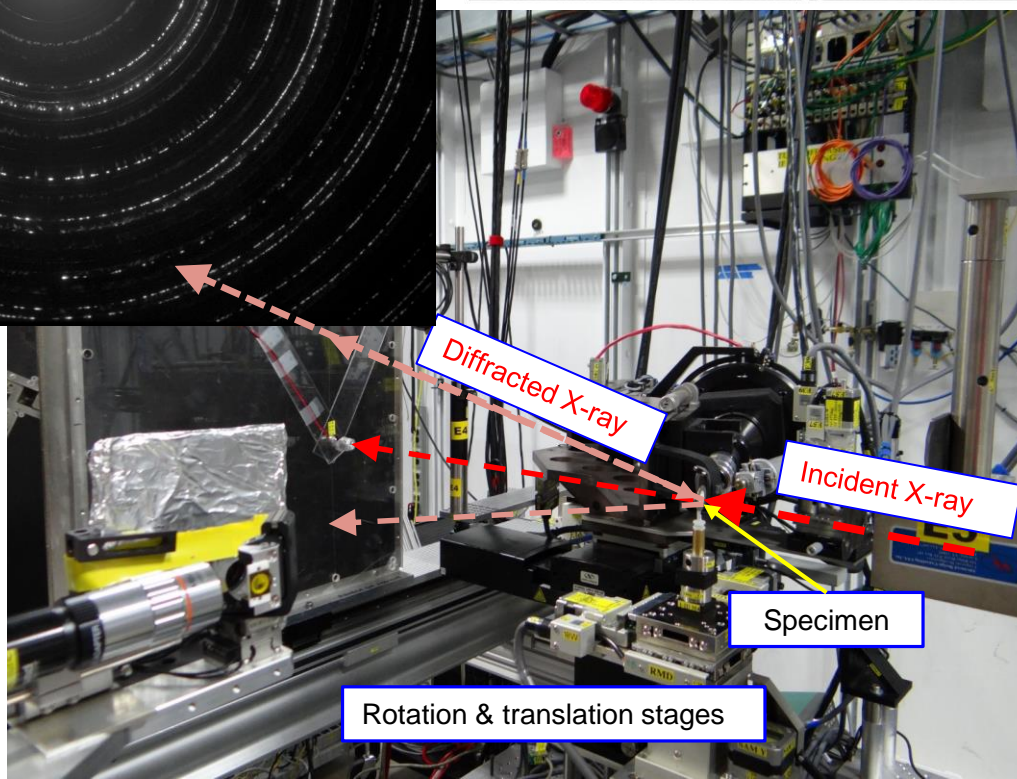
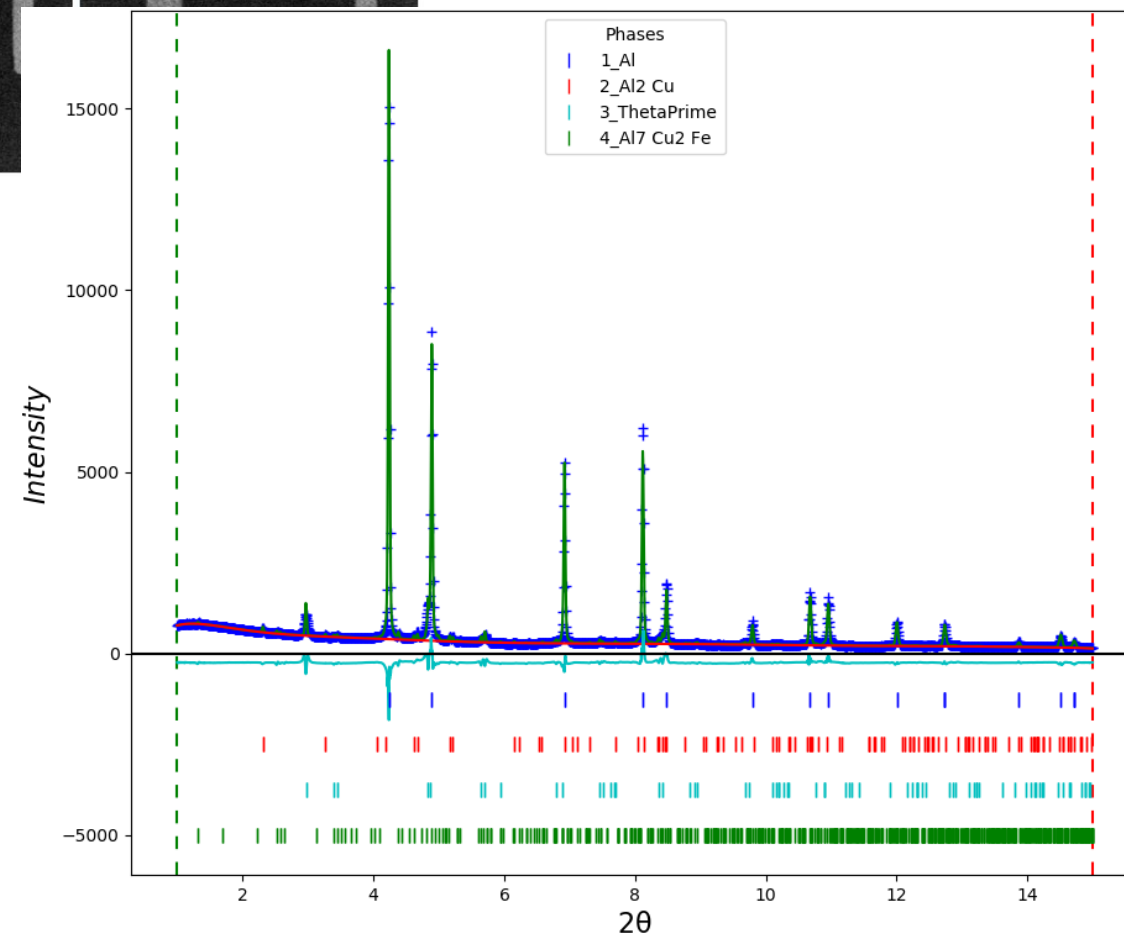
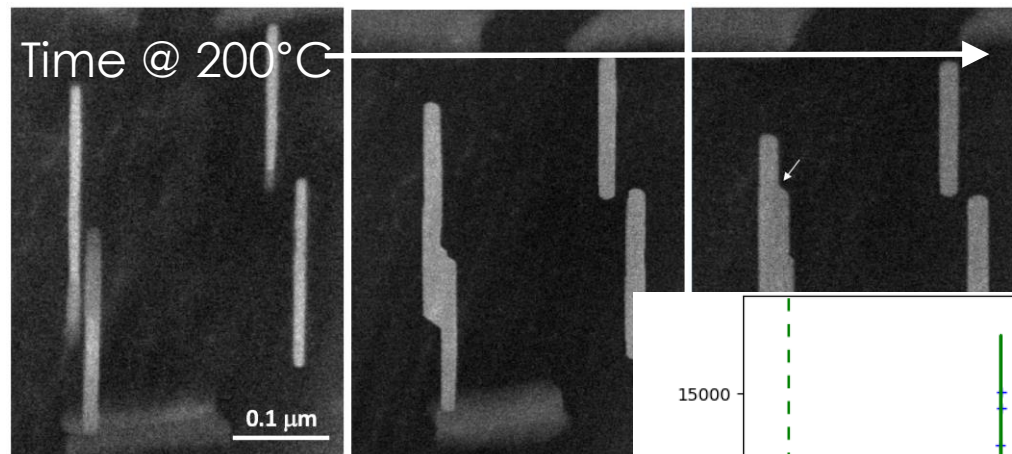
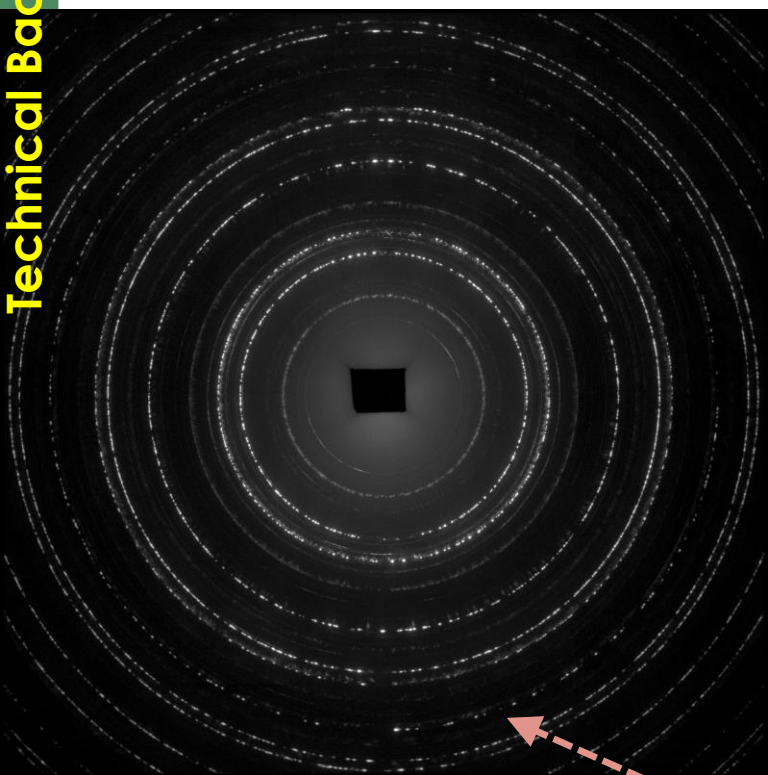


# ANL's Synchrotron x-rays allow observation of trace precipitate's growth & critical phase transformation from $\theta'$ to $\theta$ in ORNL's ACMZ related alloys

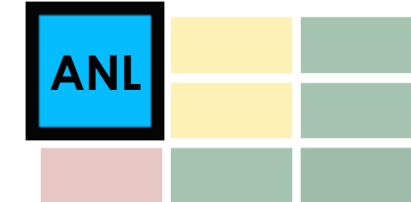


Dileep Singh, ANL  
 Andrew Chang, ANL  
 Lianghua Xiong, ANL  
 Larry Allard, ORNL  
 Amit Shyam, ORNL  
 Thomas Watkins, ORNL  
 Subtask 1A

**Matrix**



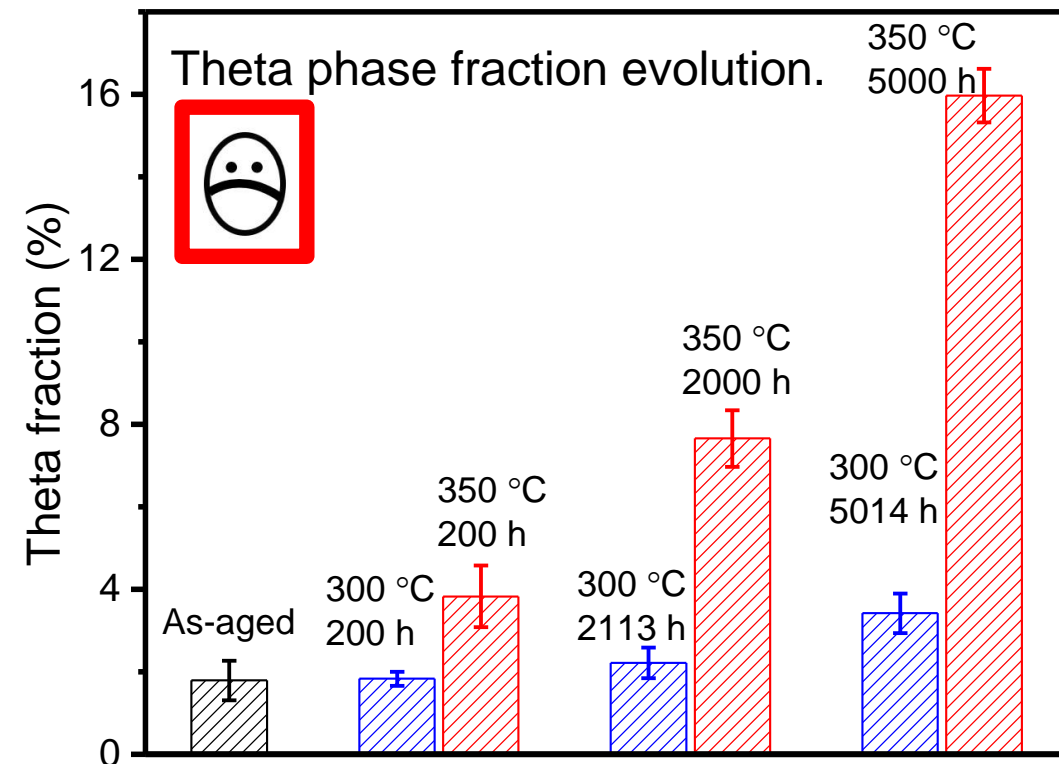
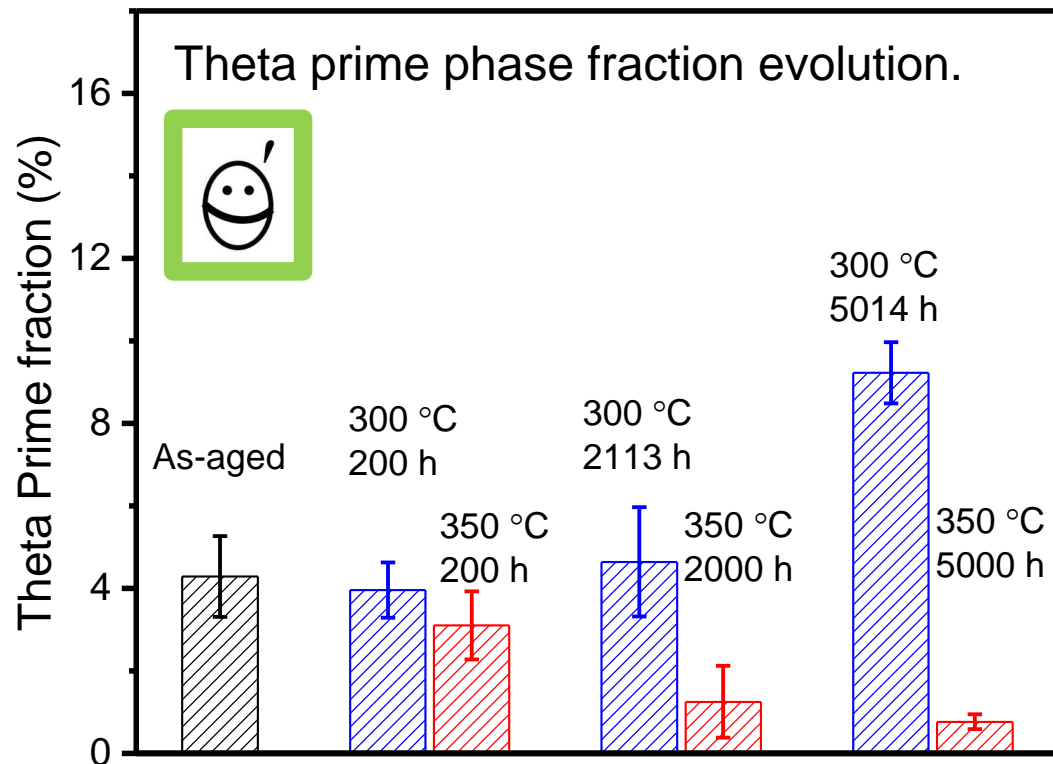
# Trace precipitate's growth & critical phase transition from $\theta'$ to $\theta$ quantified for ORNL's ACMZ related alloys at ANL's APS



Matrix

T1

Dileep Singh, ANL  
Andrew Chang, ANL  
Lianghua Xiong, ANL  
Amit Shyam, ORNL  
Thomas Watkins, ORNL  
Subtask 1A

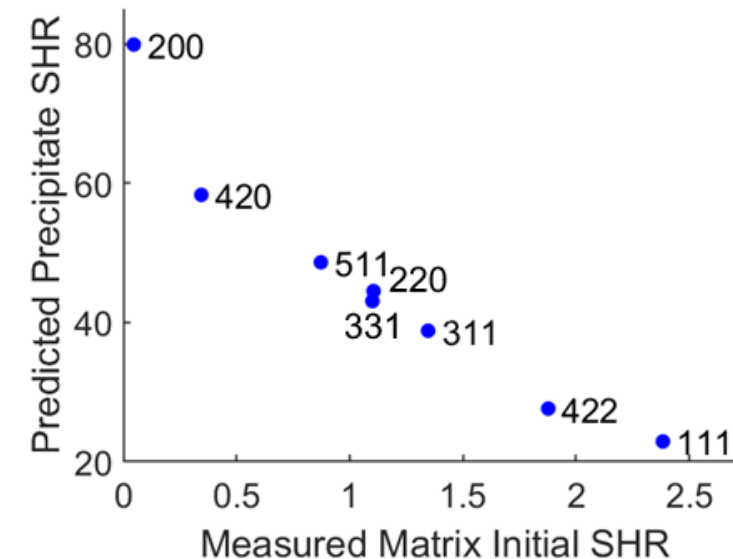
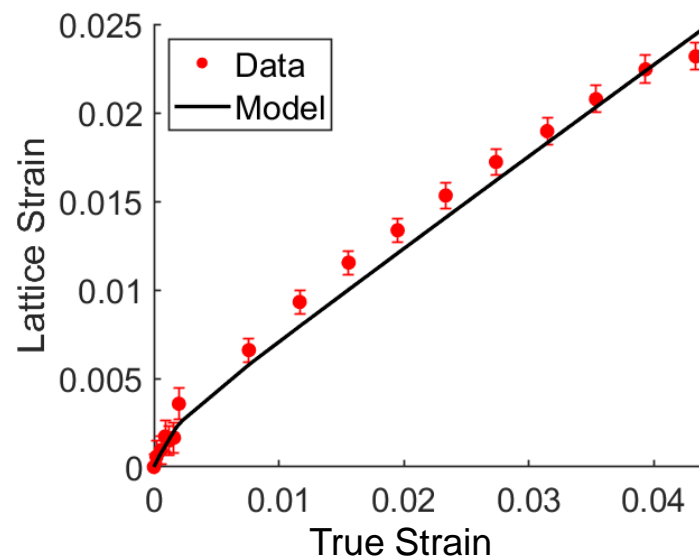
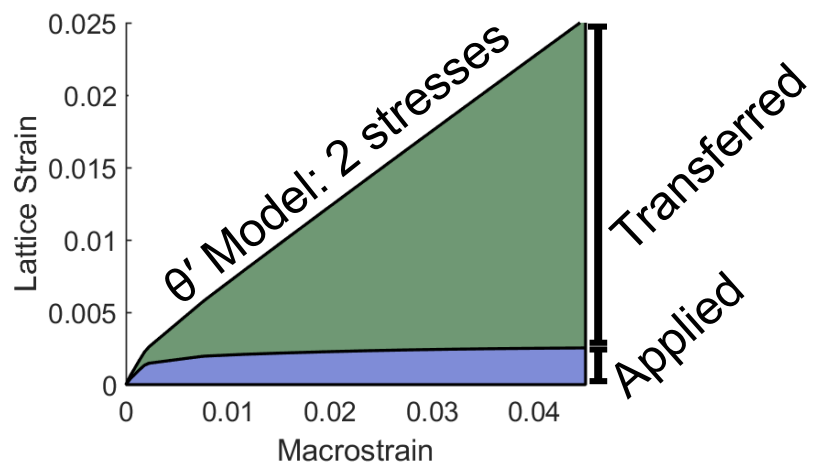
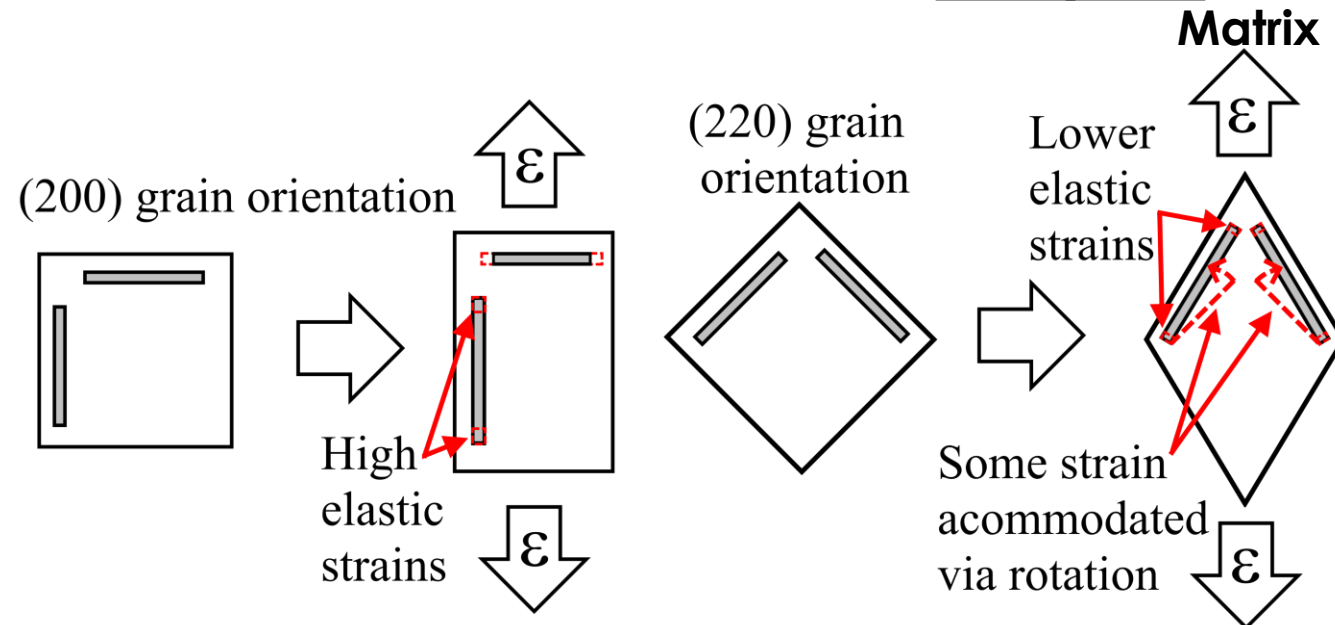
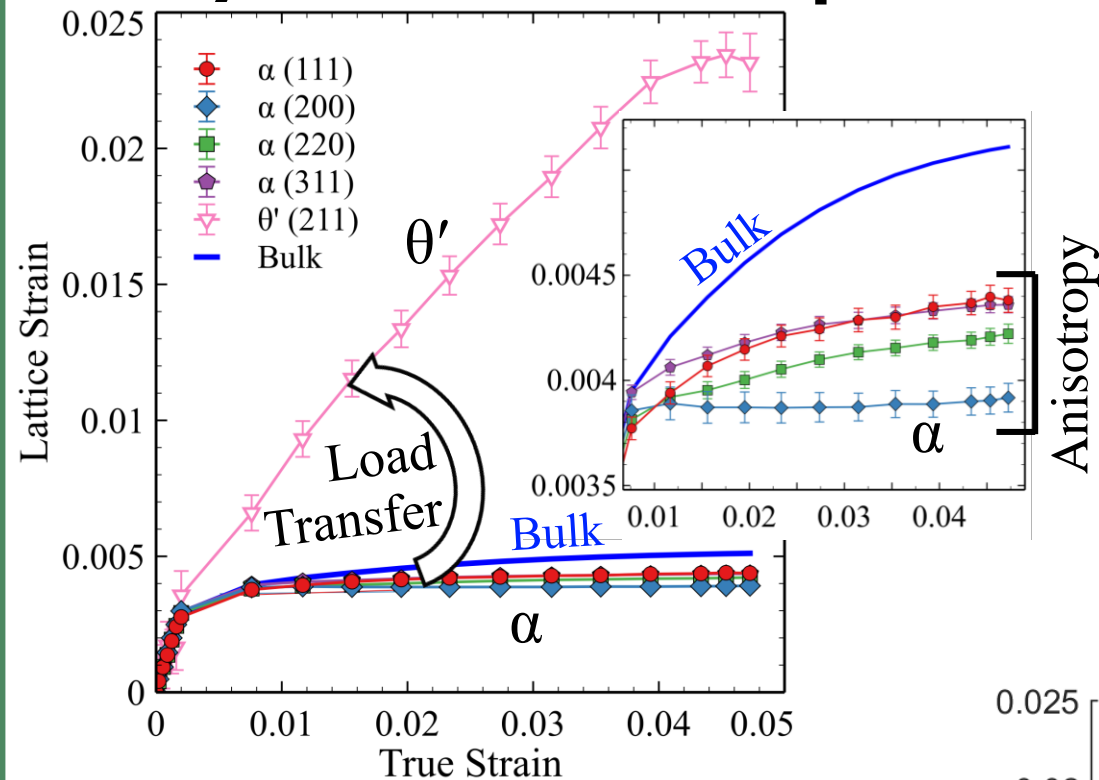


$\theta'$  –  $\theta$  fraction evolution in Al<sub>7</sub>Cu There is an apparent mechanism transition between 300 and 350°C

# Anisotropic Strain Hardening in Alloys with $\theta'$ Precipitates

T1

Brian Milligan, ORNL  
Amit Shyam, ORNL  
Dong Ma, ORNL  
Subtask 1B

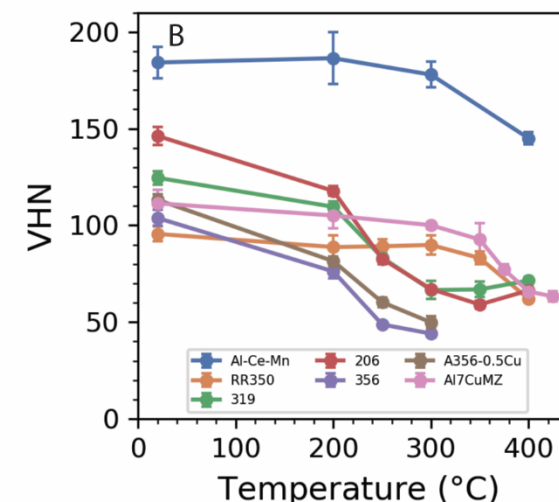
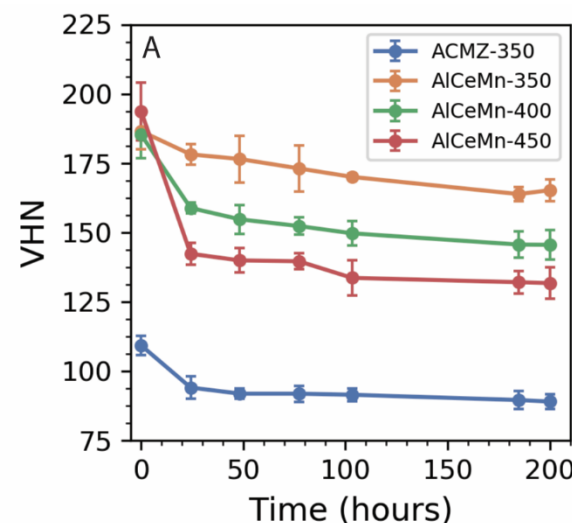
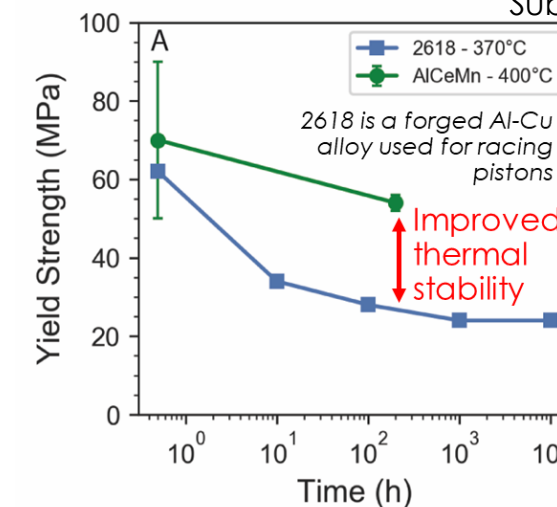
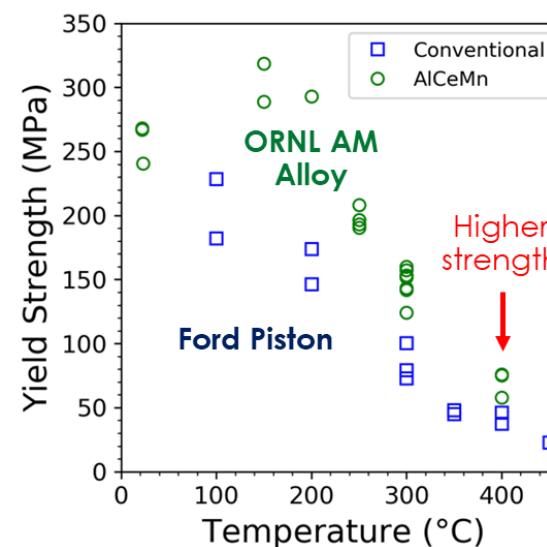


# Al-Ce-Mn – Mechanical Properties



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Subtask 3A

- Excellent high temperature strength
- Good retention of strength after extended thermal exposure
- Compares extremely well to cast alloy counterparts



Condition	YS (MPa)	Elongation (%)
As-fabricated - RT	268 ± 15	1.14 ± 0.83
As-fabricated - 400°C	70 ± 20	14.5 ± 3.7
Pre-conditioned - 400°C	54 ± 2	43.5 ± 6.3